Report for 2004ME29B: Metal mobilization from municipal biosolids stockpiles: The role of dissolved organic matter.

- Other Publications:
  - Peckenham, J., J. Nadeau, A. Amirbahman, W. Brutsaert, and J. Wilson, 2004, Leachate From Biosolid Stockpiles: Nutrients and Metal Mobility , Amer. Geophys. Union Ann. Mtg., Montreal, May 2004.
  - Peckenham, J., J. Nadeau, and A. Amirbahman, 2004 Nitrogen loss from biosolids stockpiles, Maine Water Conference, April 2004.
  - Nadeau J., J. Peckenham, and A. Amirbahman, 2004 Trace Metal Movement from Field Stacked Biosolids, Maine Water Conference, April 2004.

Report Follows

Interim Project Report to the USGS-WRRI:

Metal and Phosphorus Mobilization from Municipal Biosolids Stockpiles: Field Experiments

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Abstract

Trace metal and phosphorus (P) release, fractionation, and loading from Class B lime-stabilized biosolids that were field stacked for 100 days were evaluated. The biosolids were stacked on a lined cell plot ($3.6 \times 22.5 \times 0.6$ m) and a zero-tension pan lysimeter plot ($6 \times 15 \times 0.6$ m) to evaluate the movement of trace metals and P through the biosolids stockpile, and the underlying soil, respectively. Metals and P were analyzed for their total concentration, as well their size fractionation. Cumulative loadings of six regulated metals in Maine, over 90 days were as follows: As, 5.35 kg/ha; Cd, 0.031 kg/ha; Cu, 0.97 kg/ha; Ni, 1.27 kg/ha; Se, 0.52 kg/ha; Zn, 0.37 kg/ha. Stated as a percent of the Maine Revised Statutes Annotated (MRSA) Chapter 419 annual loading limits these were, As, 1070%; Cd, 1.6%; Cu, 1.3%; Ni, 6.4%; Se, 10.4%; Zn, 0.3%. Ultrafiltration of the leachate from the lined biosolids stockpile showed Al, As, Cd, Cr, and Cu to be mostly dissolved (MW cutoff < 1000 Da), and Fe, Mn and P to be predominantly colloidal (MW > 1,000 Da). Zero-tension pan lysimeters were placed at depths of 30, 60 and 90 cm below the biosolids stockpile. Peak average concentrations at 90 cm during a one year period were As, 654 µg/L; Cd, 19.5 µg/L; Cu 4820 µg/L; Ni, 49 µg/L; Se, 249 µg/L; Zn, 304 µg/L. Ultrafiltration of lysimeter filtrates showed metals to be predominantly dissolved (MW cutoff < 1000 Daltons), suggesting that most colloidal trace metals are removed by the aquifer material.

1.1 Introduction

Biosolids are derived from sewage after the addition of coagulants and flocculants to wastewater. Biosolids stockpiling is necessary for the efficient utilization of the sewage sludge residuals in agricultural practice. Field stacking is common, where biosolids are stored on an open field for up to 8 months [1,2]. Stockpiling options include stacking on concrete pads that may be covered or open to precipitation [1]. Stacking of biosolids on a concrete pad typically includes containment and leachate handling systems to prevent contamination of the surrounding environment.

Possible metal contamination of groundwater, due to stockpiling of biosolids, presents a special case for humans living in rural environments on or near farms with effective biosolids land spreading programs. The Maine Department of Environmental Protection (MDEP) in MRSA Chapter 419, utilizing the EPA's Part 503 rule, has regulated annual metal loadings and lifetime site metal loadings from land applied biosolids for several trace metals, which are shown in Table 1.1 [1]. This table is based on the EPA's risk assessment for metal concentrations and loadings in soil which have been determined as safe for human health. Some of the basic assumptions used in these risk assessments include organic content of biosolids, speciation of the metals and the relative availability of the metals for leaching [2].

The EPA in the part 503 rules states that the risk assessment undertaken for biosolids utilized a scientific approach "to determine acceptable environmental change when biosolids are used or disposed." Acceptable change means that even though environmental changes have occurred public health and safety is still protected. The EPA

Table 1.1 – Annual metal loading and lifetime site loading limits from land applied biosolids in Maine (MRSA Chapter 419)

	As	Cd	Cu	Pb	Ni	Se	Zn
Maximum Annual Loading (kg/ha)	0.5	1.9	75	15	20	5	140
Maximum Lifetime Site Loading (kg/ha)	10	39	1500	300	420	100	2800

in part 503 identified 14 exposure pathways associated with biosolids [2]. It was noted in the revision of the exposure pathways for groundwater, surface water and air that better fate and transport models and assumptions as to how much of a pollutant was released from the biosolids was needed [2].

Trace metal release from biosolids has been linked to microbiological activity [3], water solubility [4] and breakdown of organic compounds that bind metals in the soil [5]. McBride et al. showed that shallow groundwater collected via tension lysimeters from an experimental plot that had a one time treatment (high dosage) of biosolids 15 years prior had elevated levels of several trace metals when compared to a nearby control plot that had received no biosolids application [6]. Richards et al. found elevated trace metal levels such as Cd, Ni, Zn and B in soil pore water of a site treated with biosolids 20 years earlier [7,8].

Material balance, as a method of accounting for all the metals in land applied biosolids, has yielded varying results. A basic assumption by the EPA in establishing the part 503 trace metal loading limits was that due to the high organic content of biosolids and the inherent binding properties of organic matter, metal leaching from biosolids was

not of concern [3]. Baveye et al reported losses of 36% to 60% for trace metals in biosolids-amended soils tested to depths of 75 cm [9]. Similar results documenting large fractions of unaccounted for trace metals are reported by Richards et al [7], Dowdy et al [10], Chang et al [11], and Bell et al [12]. Reasons cited for these discrepancies include deficiencies in the analytical extraction methods [10] and lateral dispersion coupled with soil erosion [13]. In a long term study conducted by Bergkvist et al, it was found that 99% of the cadmium applied via bi-annual biosolids applications spanning 41 years was accounted for in the top 17 cm of the soil profile [14]. By contrast, Yingming and Corey found only 15% of the applied cadmium from biosolids remained in the topsoil after 11 years [15].

Data concerning release of trace metals and P from stockpiled biosolids are lacking. This work focuses on measuring the concentrations, loading rates, cumulative loadings, and evaluating the size fractionation of trace metals and P in the stockpiled biosolids leachate and filtrate in the underlying soil column sampled by pan lysimeters. Zero tension pan lysimeter results are analyzed and set the stage for further experimental studies, which measure the mobility of trace metals and P through a laboratory soil column. It must be stressed that the data presented here are for stockpiled biosolids, and not for well-managed land application of biosolids and soil amendments.

Metals presented and discussed in this work include As, Cd, Cu, Ni, Se and Zn. These metals were chosen because MRSA Chapter 419 has set annual and lifetime loading limits on these metals from land applied biosolids. Loadings of the above metals can be directly compared to statutory limits. Additionally, Al, Fe, Mn and P data are presented. While these metals are not considered toxic, they have been associated with

mobility and immobility of other elements such as As. Aluminum, Fe, and Mn form

(oxy-)hydroxides that coat soil particles and remove metals and P from solution through

sorption. Mineral (oxy-)hydroxides are themselves subject to acid and reductive

dissolution, thus becoming mobile and also releasing other elements that were in the

matrix [16,17].

1.2 Materials and Methods

The experimental set-up, sample collection, handling and compositing

procedures are described in the forthcoming MS thesis by J.A. Nadeau. The

experimental set-up included 1) a lined cell ($3.6 \times 22.5 \times 0.6$ m) with an impermeable

geo-membrane designed to collect leachate through the stockpile, and 2) a zero tension

pan lysimeter plot ($6 \times 15 \times 0.6$ m) that collected filtrate passing through a soil column at

30, 60 and 90 cm depths under an unlined stack of biosolids. Trace metal and cumulative

loadings were based on trace metal concentrations determined by ICP-AES analysis of

acidified archived samples and flow measurements of the leachate from the lined cell

plot. Lysimeter trace metal concentration data were obtained from acidified archived

samples. Ultrafiltration results reported are for unacidified samples that had been

separately archived or freshly obtained in the laboratory.

Archived samples were diluted 10:1 with Nanopure® DI water and filtered

through 0.45 μm membranes. Metal concentrations were measured on a Perkin-Elmer

Optima 3300XL ICP-AES. Calibration curves of stock metal solutions were determined

prior to each run on the ICP-AES. Standard additions of a stock solution with known

metal concentrations were made to a subset of leachate samples to test the matrix effect

on the ICP-AES measurements. Previous studies by Ure [18] have found that large positive matrix or spectral interferences in water or soil extracts, and especially in soil digests, occur with ICP-AES because of the common occurrence of high concentrations of Al, Ca and Mg in these types of samples. Matrix interferences were found to be insignificant in this work for calculating the loading rates and cumulative loadings for As, Cd, Cu, Ni and Se. Significant effects were found for Zn, however the level of Zn in this study is insignificant compared to allowable limits.

Ultrafiltration experiments were performed on unacidified samples diluted in the same manner as described above. A Millipore / Amicon Model 8200 Stirred Ultrafiltration Cell utilizing cellulose membranes with pore sizes of 10,000 NMWL (10 KDa) and 1,000 NMWL (1 KDa) were used. Each filtered sample utilized the following operational procedure: 200 ml of diluted, 0.45 μm filtrate was placed in the ultrafiltration cell under an N_2 atmosphere at 50 psi. The first 100 ml of filtrate, passing the 10 KDa membrane were collected and 30 ml were taken for analysis. The remaining 70 ml was placed in the cleaned ultrafiltration cell with a 1 KDa membrane, and the procedure was repeated, where 35 ml of filtrate passing the 1 KDa membrane were collected for analysis. All ultrafiltration membranes were flushed with 100 ml of DI water prior to sample addition to remove any residual impurities on the membranes. The ultrafiltration cell was triple rinsed with DI water after each run. Sample collection glassware was acid washed and rinsed with DI water after each sample.

1.3 Results and Discussion

1.3.1 Lined Stockpile

Cumulative leachate volumes from the lined cell were measured as described in the forthcoming MS thesis by J.A. Nadeau. Concentration trends, loading rates and cumulative loadings for the leachate collected during the 100 day experiment are presented in Figures 1.1 – 1.3. The metals presented showed four distinct release patterns. Release of Al, As, P and Zn showed a steady concentration for the first 20 days followed by increase in concentration for the remaining 80 days. Release of Fe and Mn showed high concentrations up to day 30 followed by a steady low concentration for the remaining 70 days. Release of Cu and Ni showed high concentrations at day 6, then lower and consistently sustained concentrations over the remaining 94 days of the experiment. Cadmium showed an increasing concentration trend for the first 25 days followed by a decrease in concentration until day 50, and a constant increasing concentration trend until day 100. Selenium showed an increase in concentration until day 25 followed by a consistently declining concentration trend for the remaining 75 days.

Loading rates (mass/day/initial volume of biosolids) were calculated from the leachate concentration and cumulative volume data and normalized to initial biosolids volume as follows:

$$L_i = (F_i - F_{i-1}) * ((C_{j,i} + C_{j,i-1})/2)/1000 * (t_i - t_{i-1}) * V_b \quad (1)$$

Where:

L_i = Loading rate at time step i (mg/day/m^3)
F_i = Cumulative volume at time step i (L)
F_{i-1} = Cumulative volume at time step i-1 (L)
$C_{j,i}$ = Concentration of species j at time step i (µg/L)

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$C_{j,i-1}$ = Concentration of species j at time step i -1 (µg/L)
t_i = Time at time step i (d)
t_{i-1} = Time at time step i-1 (d)
V_b = Initial volume of biosolids on lined cell (m³)

Cumulative loadings were calculated as follows:

$$CL_i = CL_{i-1} + ((F_i - F_{i-1}) * ((C_{j,i} + C_{j,i-1})/2))/1000 \quad (2)$$

Where:

CL_i = Cumulative loading at time step i (mg)
CL_{i-1} = Cumulative loading at time step i-1 (mg)

Results of these calculations are presented in Figure 1.2 (loading rates) and Figure 1.3 (cumulative loadings).

Examining the graphs in Figures 1.2 and 1.3 one can observe that the loading rate and cumulative loadings for Al, As, Cd, Cu, Ni, P, Se and Zn all appear to have similar behavior suggesting that the leachate flow is driving the loading rate and cumulative loadings. The Fe and Mn data, however, show a behavior different from the other metals. Loading rates (Fig 1.2) all appear to peak around day 30 and decline for the remaining 70 days of the experiment.

Figure 1.1 – Lined cell leachate temporal trace metal concentration

Concentration Trend Al, As and P

Concentration Trend Cu, Ni and Zn

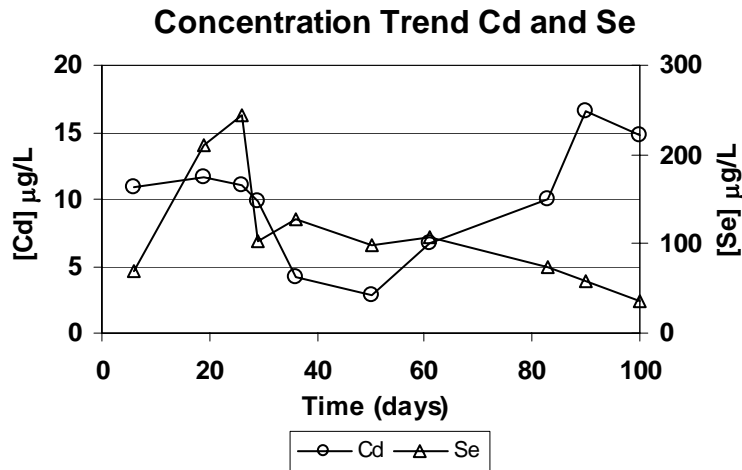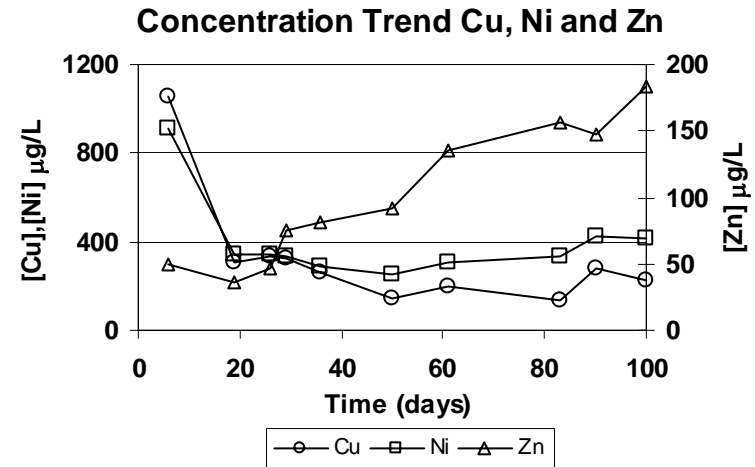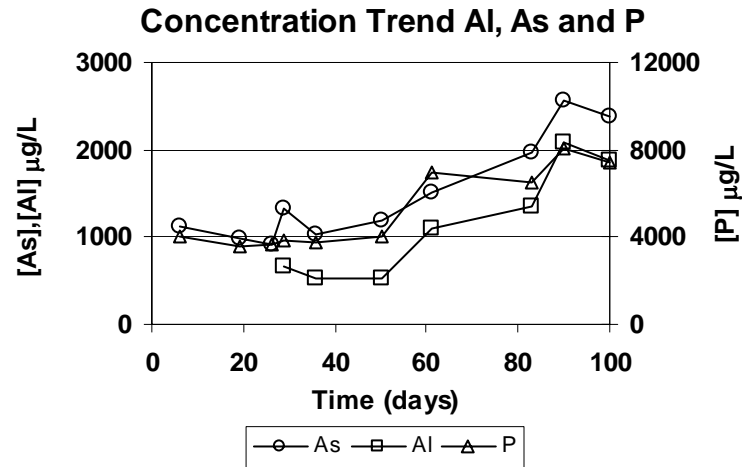Concentration Trend Cd and Se

Concentration Trend Fe and Mn

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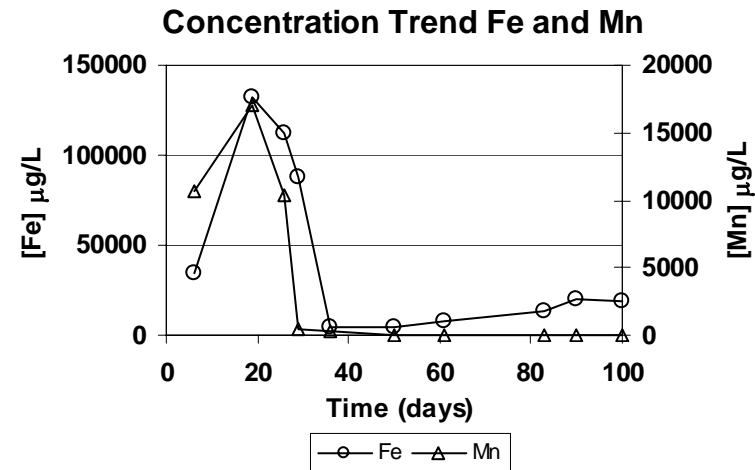
Figure 1.2 – Lined cell leachate metal temporal loading rates

Loading Rates As, Al and P

Loading Rates Cu,Ni and Se

Loading Rates Cd and Zn

Loading Rates Fe and Mn
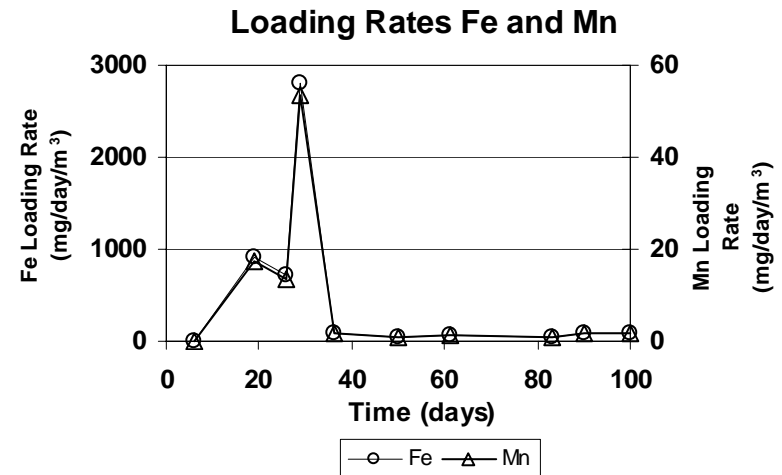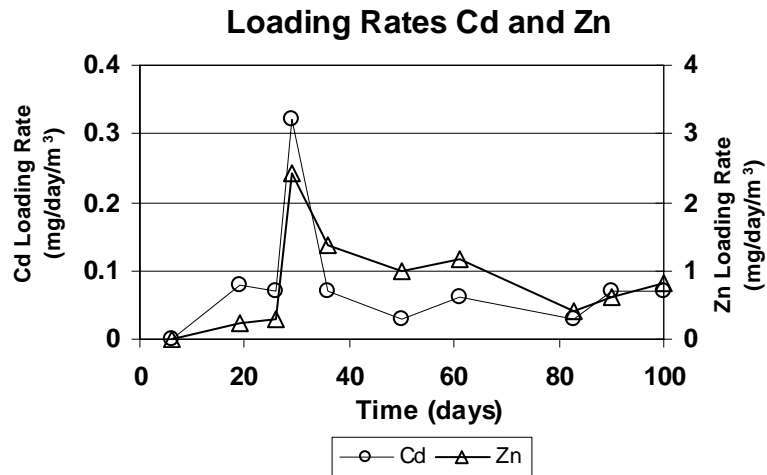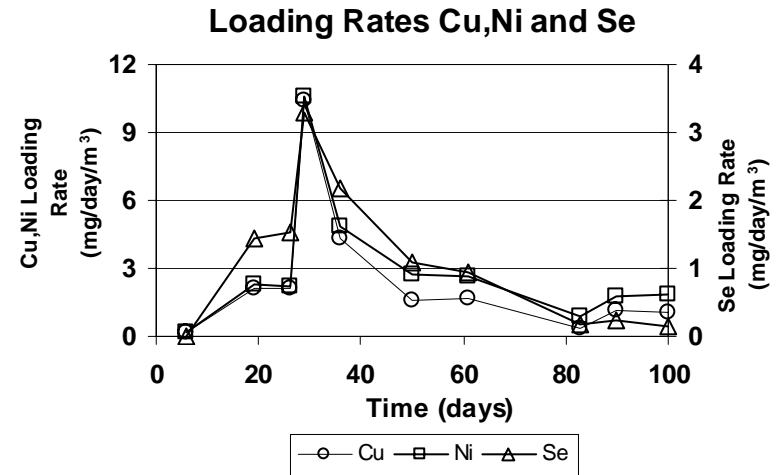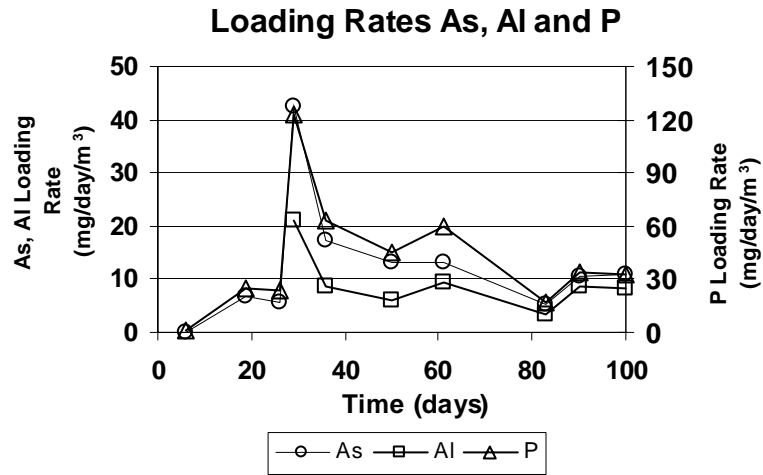
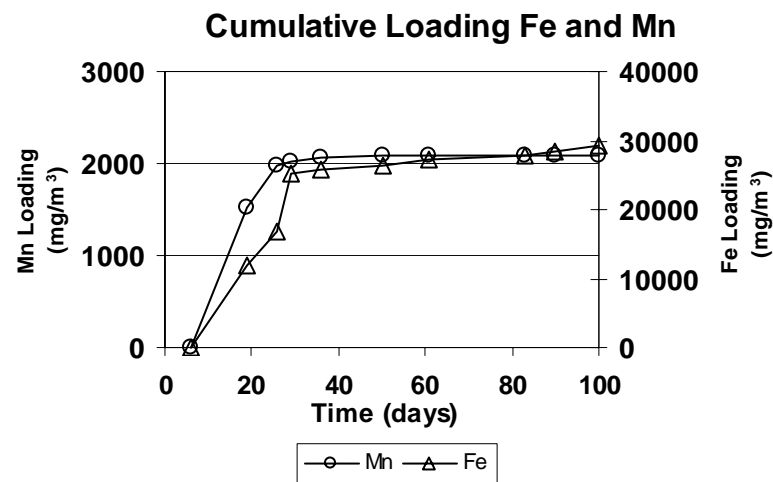**Figure 1.3 – Lined cell leachate metal cumulative loading rates**

Cumulative Loading Al, As and P

Cumulative Loading Cu and Ni

Cumulative Loading Cd, Se and Zn

Cumulative Loading Fe and Mn

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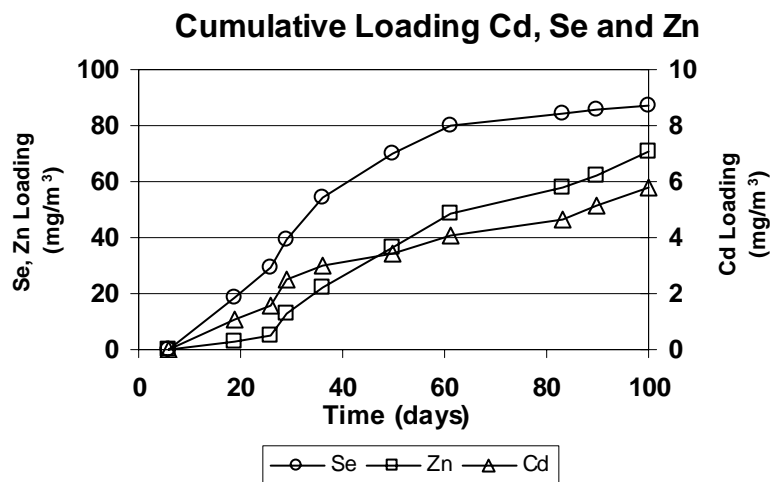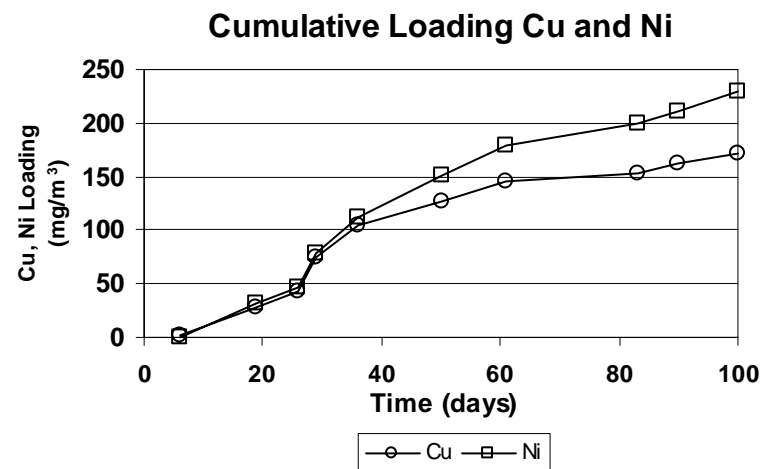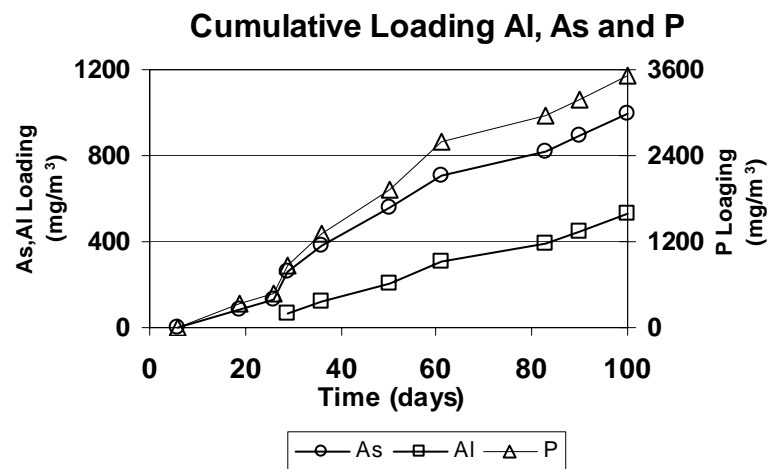
Comparison of the cumulative loadings of As, Cd, Cu, Ni, Se and Zn at day 90, scaled from a kg/m^3 to kg/ha (1 ha of biosolids with a depth of 0.6 m) for direct comparison to the MRSA Chapter 419 statutory limits in Table 1.1 are presented in Table 1.2. Included in Table 1.2 is the ratio in percentage of the 90 day loadings to the total annual loading limit. Based on the results shown in Table 1.2 all of the regulated metals released from the stockpiled biosolids are below the Chapter 419 annual loading limits except for As at 90 days. If one were to extrapolate from day 90 to day 240 (8 months, maximum allowable field stacking duration) in a linear fashion, all of the regulated metals in Table 1.2, with the exception of As, would still be below the annual loading limits.

Table 1.2 – Comparison of 90 day metal loadings and annual metal loading limits

	Calculated 90 Day Loading (kg/ha)	Maximum Annual Loading (kg/ha)	% of Allowable Annual Loading
Arsenic	5.35	0.5	1070
Cadmium	0.031	1.9	1.6
Copper	0.97	75	1.3
Nickel	1.27	20	6.4
Selenium	0.52	5	10.4
Zinc	0.37	140	0.3

1.3.2 Lysimeter Stockpile

Lysimeter data are presented in two parts, 1) average concentrations (composite samples) at a given depth over time, and 2) one sampling round showing results of each of the 15 individual lysimeter pans sampled. The four dates shown in the average lysimeter concentration data span over one year and do not include the standard deviation error bars. The reason for this is that on two of the sampling dates (Sep-03 and May-04) only a composite sample for each depth was analyzed, while the Jun-03 and Jul-04 samples had each individual lysimeter analyzed. When standard deviations at a given

depth are calculated using the Jun-03 or Jul-04 data, they are often larger than the average, indicating a wide spread in the concentrations at the same depth. Loading rates for the lysimeters cannot be calculated because flow to the lysimeter pans was not measured. Therefore, we report concentration data at three depths over time in an effort to assess movement of trace metals from the biosolids.

Concentrations of As, Cd, Cu, Ni, Se and Zn collected in the pan lysimeters are presented in Figure 1.4. The original stockpile was emplaced in December 2002 and removed on the day the June 2003 samples were taken. The stockpile was replaced with fresh biosolids in July 9, 2003 and removed June 15, 2004. A notable increase in Cu and Zn between Jun-03 and Sep-03 is observed. This may be attributed to higher levels of Cu and Zn in the biosolids stacked July 9 in comparison to the December 2002 biosolids.

Arsenic concentrations show a steady increase over time but with higher concentrations with depth. Copper concentrations show a steady decreasing trend from Sep-03 until Jul-04 with higher concentrations with depth. In contrast, P and Se concentrations increase over time and decrease with depth. If the only source of a contaminant were from the leachate, one would expect the response shown by P and Se. The response of As and Cu leads one to suspect that additional mechanisms, such as the dissolution of Al, Fe and Mn (oxy-hydr)oxides, may be occurring. The dissolution of these minerals may release the adsorbed metals such as As and Cu. Alternatively, the adsorbed As and P may be desorbed via ligand exchange with the organic matter. Analysis of soil samples at Highmoor Farm showed As and Cu concentrations of 6.1 μg/g and 14.3 μg/g respectively. No Se was detected in the soil, and thus, the only source of this element is the biosolids that further supporting the decreasing concentration of Se

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with depth. Dissolution of Fe and subsequent release of As from a landfill contaminated aquifer has been reported by Welch and Stollenwerk [19]. Concentrations of Cd and Ni remain relatively constant over time. The increasing concentration trends of As, P and Se, suggest possible transport implications which will be explored and discussed in the final report.

Individual pan lysimeter results are presented for the June-03 samples in Table 1.3. Large differences in concentrations at the same depth exist. The existence of preferential flow paths is suspected.

Figure 1.4 – Zero tension pan lysimeter temporal average concentrations of As, Cd, Cu, Ni, Se and Zn at depth

Arsenic Trend

Cadmium Trend
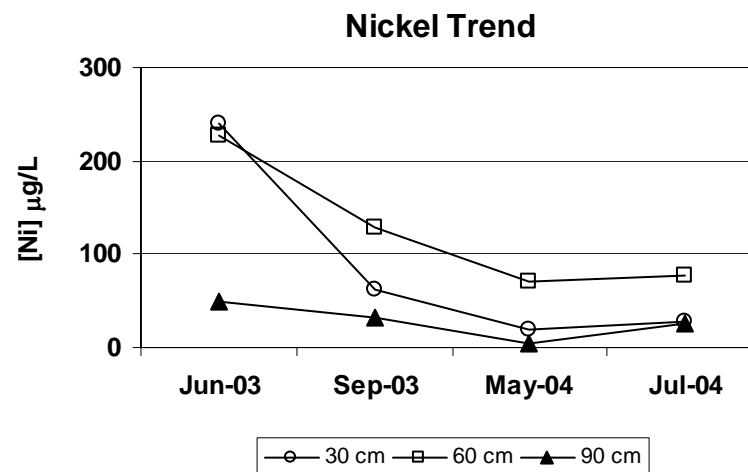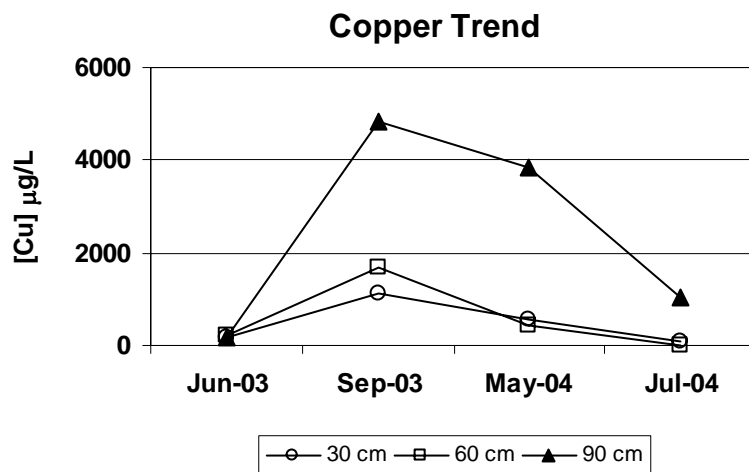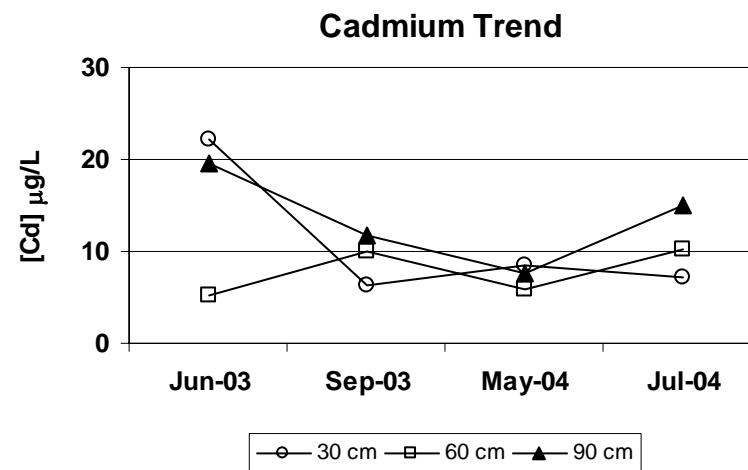

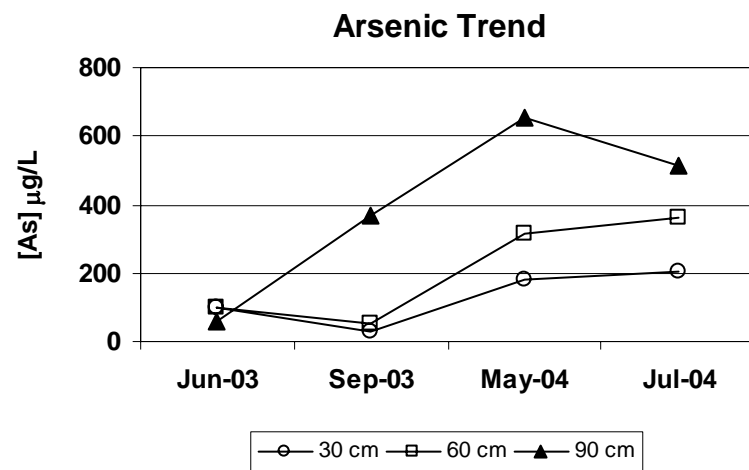Copper Trend

Nickel Trend

Figure 1.4 (continued) – Zero tension pan lysimeter average concentrations of As, Cd, Cu, Ni, Se and Zn at depth over time

Selenium Trend

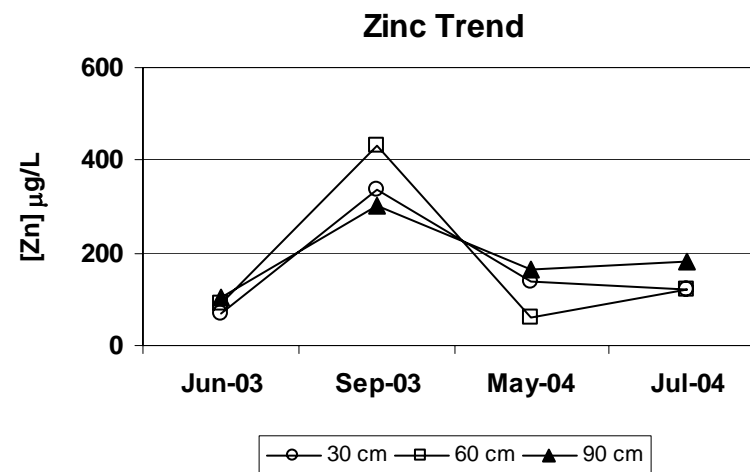

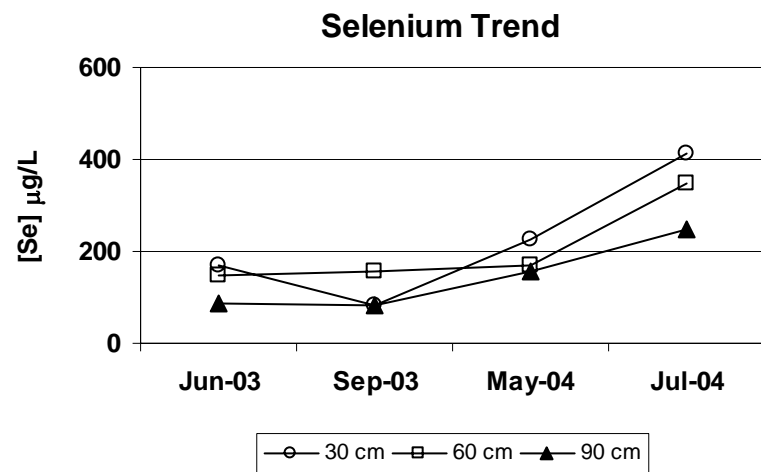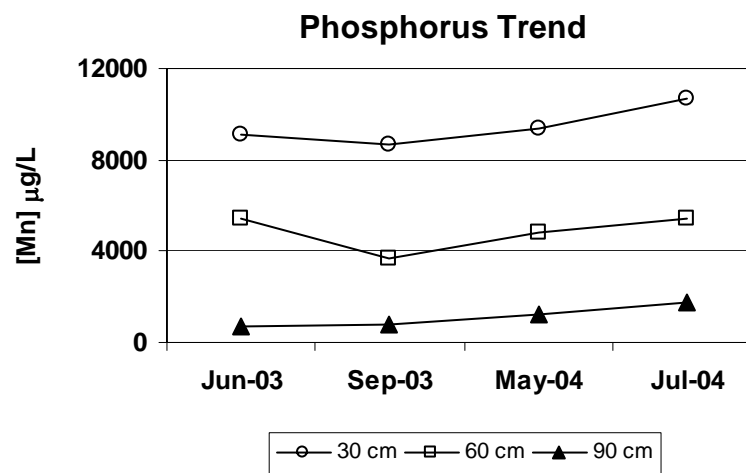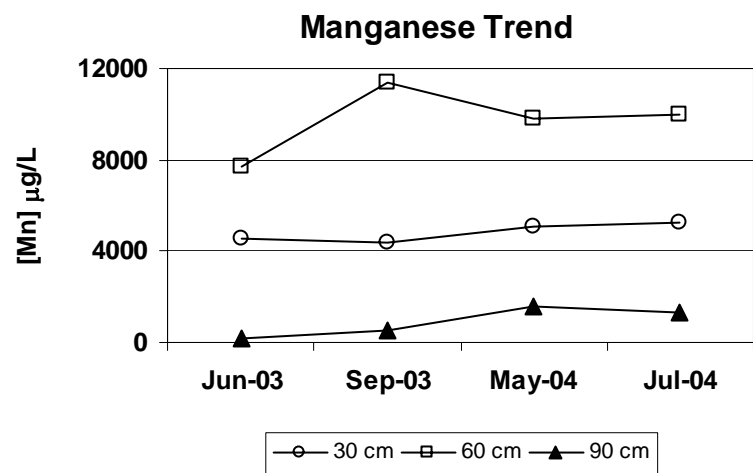Zinc Trend

Figure 1.5 - Zero tension pan lysimeter temporal average concentrations of Al, Fe, Mn and P at depth

Aluminum Trend

Iron Trend

Manganese Trend

Phosphorus Trend
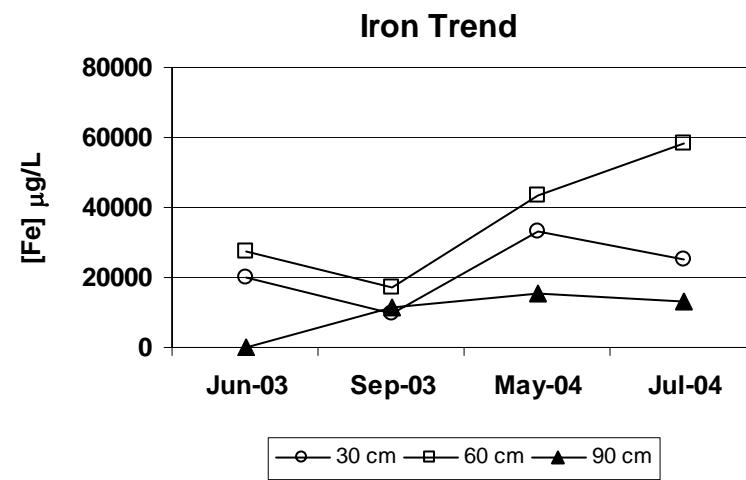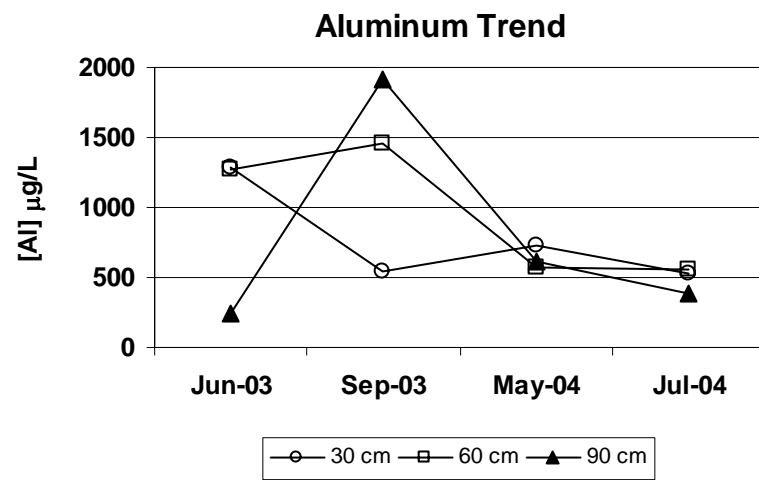
Table 1.3 – Zero tension pan lysimeter metal concentrations June 2003

	Al (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	P (mg/L)	Se (mg/L)	Zn (mg/L)
1C1	471	23.7	40.1	236.4	537	195	35.6	2761	79.9	28.2
1C2	930	43.8	0.5	70.1	41370	9415	145.8	2956	118.1	42.9
1C3	1613	128.0	8.1	291.8	10558	3564	307.6	10919	263.0	84.4
1E1	140	1.8	58.7	18.7	55	0	0	144	3.3	11.7
1E2	3248	302.2	3.4	167.5	47905	5049	474.1	28686	391.0	175.0
2C1	2518	267.7	8.5	246.6	53898	44032	500.4	21265	286.6	171.6
2C2	488	38.5	12.9	167.3	428	1184	82.3	1255	99.6	20.8
2C3	156	33.8	4.4	89.2	133	53	0.5	464	36.4	20.2
2E1	2802	134.5	0.4	507.8	82732	32654	514.4	3273	244.5	214.9
2E2	385	31.1	0	99.2	328	230	36.4	881	78.3	21.1
3C1	116	58.9	38.6	0.9	12	0	0	286	55.4	232.8
3C2	631	123.9	6.6	513.3	551	447	136.6	2165	194.2	115.0
3C3	135	33.7	36.7	17.5	31	0	0	112	59.4	78.1
3E1	179	60.0	9.6	14.8	76	5	0.5	670	64.0	43.6
3E2	156	26.9	5.8	23.9	84	14	10.0	121	57.1	45.0

Note: 1=30 cm depth, 2= 60 cm depth and 3=90 cm depth. Letters C=center and E= edge Numbers 1,2 and 3 were assigned to each lysimeter at a given depth for consistent lysimeter filtrate tracking over time.

1.3.3 Ultrafiltration

A comparison of ultrafiltration results between the aged leachate (sampled August 2003 and ultrafiltered March 2004) and fresh leachate (sampled May 2004 and ultrafiltered within 10 days) is presented in Table 1.4. Increases in the colloidal fraction (MW cutoff > 1,000) are noted for Fe, Ni, Se, Zn and DOC with aging. The majority of the Al, As, Cd, and Cu pass the MW 1 KDa filter and could be operationally defined as truly dissolved [20], while Fe, Mn and P may be operationally defined as colloidal (size fraction less than 0.45 μm and larger than 1 KDa).

Table 1.4 – Lined cell leachate Ultrafiltration comparisons

Metal	Aged Leachate		Fresh Leachate	
	% Passing 10 Kilodaltons	% Passing 1 Kilodalton	% Passing 10 Kilodaltons	% Passing 1 Kilodalton
Aluminum	92	92	87	62
Arsenic	92	70	81	66
Cadmium	99	84	93	82
Copper	92	90	-	-
Iron	7	2	33	3
Manganese	0	0	0	0
Nickel	45	8	86	20
Selenium	65	51	80	67
Zinc	64	30	96	48
Phosphorus	12	5	-	-
DOC	58	40	94	92

Jensen and Christensen studied the physical size and colloidal nature of metals found in leachate from landfills [20]. Species passing the 1 KDa (MW < 1,000) membrane were defined as truly dissolved and anything larger as colloidal. The findings of this study were that 78-95% of the metals (Cd, Cu, K, Mg, Na, Ni, Pb and Zn) were truly dissolved, while Ca and Mn were evenly split between colloidal and dissolved fractions, and Fe was 85% colloidal. Upon aging, DOC becomes more colloidal when

compared to fresh leachate. Possible reasons for this include polymerization of the DOC

into larger molecules [16], an increase in the percentage of larger sized DOC through the

degradation of the smaller, simpler molecules by biological activity, and differences in

the character of DOC released from the stockpile as a function of biosolids age. In

contrast, the species in the filtrate from the lysimeters (Table 1.5) appear to be mainly

dissolved, with the exception of P, which may be attributed primarily to the filtration of

the colloidal sized materials by the soil column.

Table 1.5 – Zero tension pan lysimeter filtrate Ultrafiltration comparisons

| | Lysimeter 1-C 6/2003 | | Lysimeter 2-A 6/2003 | |
Metal	% Passing 10 Kilodaltons	% Passing 1 Kilodalton	% Passing 10 Kilodaltons	% Passing 1 Kilodalton
Aluminum	77	45	97	66
Arsenic	92	89	93	78
Cadmium	72	70	98	84
Copper	82	79	89	71
Iron	84	75	94	75
Manganese	87	74	95	76
Selenium	90	87	99	80
Zinc	97	82	98	86
Phosphorus	16	9	80	62
DOC	72	-	82	74

1.4 Conclusions

The results of this study indicate that As released from a lime-stabilized Class B

biosolids stockpile during the first 90 days exceeded the annual loading limits for land-

applied biosolids by an order of magnitude and equaled the lifetime loading limit.

Arsenic release data from the lined stockpile also showed a consistently increasing trend

in concentration over time suggesting that the biosolids are an important source of As.

The other controlled metals studied (Cd, Cu, Ni, Se and Zn) were released during the first

90 days of stockpiling at rates ranging from 0.3% to 10.6% of the MRSA Chapter 419 annual limits.

Lysimeter data showed the oxyanions As, P and Se to be mobile through the soil column. Phosphorus and Se concentrations increased with time and decreased with increasing depth as one might expect if their source was the leachate leaving the stockpile and traveling through the soil column. Arsenic concentration in the lysimeters increased with time and with depth. To explain this behavior, another transport and release mechanism such as ligand exchange involving the leachate DOC, or the reductive dissolution of the minerals must be considered. Ultrafiltration of the lined cell leachate showed significant colloidal fractions (MW>1,000 Da) of Fe, Ni, Se, Zn and DOC. Ultrafiltration of the lysimeter leachate, however, showed all metals and DOC with the exception of P to be predominantly dissolved (MW< 1,000 Da). Based on the amount of metals released from stockpiled biosolids and their mobility as determined by sampling a lysimeter plot at various depths and over time, a controlled laboratory study that will determine the mobility of trace metals in biosolids leachate were conducted. The results of this study will be presented in the final report. The high As release rate from biosolids stockpiles should be of concern and justify further laboratory and field experimentation.

1.5 References

1- MRSA Chapter 419 www.maine.gov/sos/cec/rcn/apa/06/096/096c419.doc
2- US EPA Part 503 Rule www.epa.gov/owm/mtb/biosolids/index
3- Qureshi, S.;Richards, B.K.; Hay, A.G.; Tsai, C.C., McBride, M.B.; Baveye, P. and Steenhuis, T.S.; "Effect of Microbial Activity on Trace Element Release from Sewage Sludge" ; Environmental Science and Technology 2003 37:3361-3366.
4- McBride, M.B.; "Soluble trace metals in alkaline stabilized sludge products"; Journal of Environmental Quality 1998 27:578-584

5- Martinez C.E.; Jacobson, A.R. and McBride, M.B.; "Aging and temperature effects on DOC and elemental release from metal contaminated soils"; Environmental Pollution 2003 122:135-143

6- McBride, M.B.; Richards, B.K.; Steenhuis, T. and Spiers, G.; "Long-Term Leaching of Trace Elements in a Heavily Sludge-Amended Silty Clay Loam Soil"; Soil Science Vol 164 No. 9 pp 613-623 (1999)

7- Richards, B. K.; Steenhuis, T. S.; Peverly, J. H. and McBride, M. B.; "Metal mobility at an old heavily loaded sludge application site"; Environmental Pollution Vol 99 no 3 pp 365-377 (1998)

8 - National Research Coucil; "Biosolids Applied to Land: Advancing Standards and Practices" July 2, 2002

9- Baveye, P.; McBride, M.B.; Bouldin, D.; Hinsley, T.D.; Dahdoh, M.S.A. and Abdel-sabour, M.F.; "Mass balance and distribution of sludge-bourne trace elements in a silt loam soil following long-term applications of sewage sludge"; The Science of the Total Environment 227 (1999) 13-28

10- Dowdy, R.H.; Latterell, T.D.; Hinesly, R. B.; Grussman, R.B. and Sullivan, D.L.; "Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications"; Journal of Environmental Quality 20: 119-123.

11– Chang, A.C.; Warneke, J.W.; Page, A.L. and Lund, L.J.; "Accumulation of heavy metals in sewage-sludge treated soils" Journal of Environmental Quality 1984 13:87-91

12– Bell, P.F.; James, B.R. and Chaney, R.L.; "Heavy metal extractability in long-term sewage sludge and metal salt-amended soils"; Journal of Environmental Quality 1991 20:481-486

13– McGrath, S.P. and Lane, P.W.; "An explanation for the apparent loss of metal in a long-term field experiment with sewage sludge"; Environmental Pollution 1989 60:235-256.

14- Bergkvist, P.; Jarvis, N.; Berggren, D. and Carlgren, K.; "Long-term effects of sewage sludge applications on soil properties, cadmium availability and distribution in arable soil"; Agriculture, Ecosystems and Environment 2111 (2003) 1-13

15– Yingming, L. and Corey, R.B.; "Redistribution of soil-borne cadmium copper and zinc in a cultivated plot"; Journal of Environmental Quality 1993 22:1-8

16- Redman, A.D., MaCalady, D.L., and Ahmann, D.; "Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite" ; Environmental Science and Technology 2002 36:2889-2896.

17- Lin, H.T.; Wang, M.C. and Li, G.C.; "Complexation of arsenate with humic substance in water extract of compost" Chemosphere 56(2004) 1105-1112.

18- Ure, A.M.; "Methods of Analysis for Heavy Metals in Soils"; Heavy Metals in Soils (Ed B.J. Alloway) Glasgow Blackie 1990

19- "Arsenic in Ground Water" edited by, A.H. Welch and K.G. Stollenwerk. Kluwer Academic Publishers 2003. Chapter 13 "Natural Remediation Potential of Arsenic Contaminated Ground Water" pages 351-380.

20- Jensen, Dorthe L. and Christensen, Thomas H.; "Colloidal and dissolved metals in leachates from four Danish landfills"; Water Resources Research Vol 33 No 9 pp 2139-2147 1999.